

# XPCS and the Slow Dynamics in Clay Gels

Methods to determine particle-scale motion in an aging system and what these motions teach us.

Bob Leheny

Johns Hopkins

Ranjini Bandyopadhyay

Jim Harden

Simon Mochrie

Yale

Peter Falus

Matt Borthwick

MIT

# X-ray Photon Correlation Spectroscopy

## Dynamic Light Scattering with X-rays

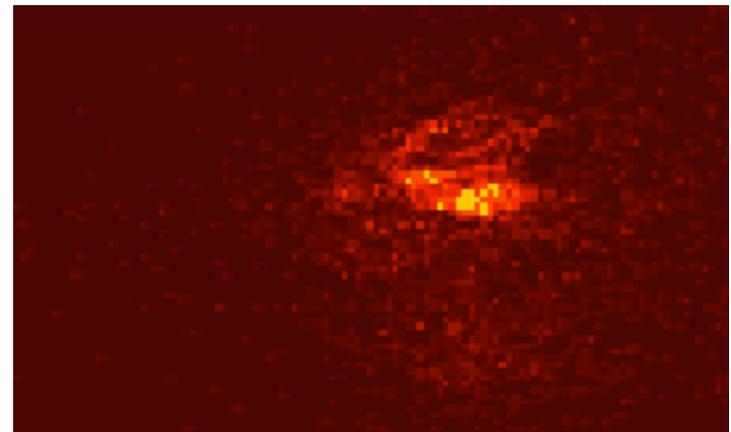
- Scattering of a Coherent Source  $\rightarrow$  Speckle
- Autocorrelation of Intensity...

$$g_2(\vec{Q}, t) = \frac{\langle I(\vec{Q}, t') I(\vec{Q}, t'+t) \rangle}{\langle I(\vec{Q}, t') \rangle^2}$$

...Gives Dynamic Structure Factor:

$$g_2(\vec{Q}, t) = 1 + \frac{\langle |S(\vec{Q}, t)|^2 \rangle}{\langle |S(\vec{Q}, 0)|^2 \rangle}$$

$\text{Co}_{0.6}\text{Ga}_{0.4}$



G. Vogl, Universität Wien

# Unique Realm of Dynamic Phase Space

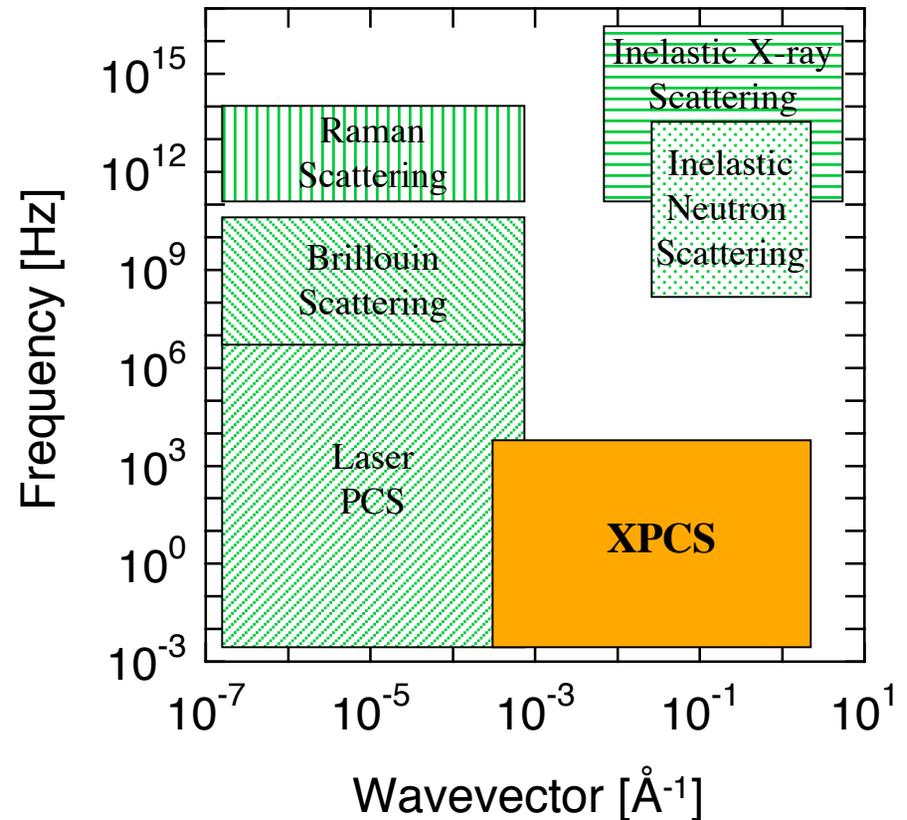
## Examples of Recent Studies:

### Small Angle

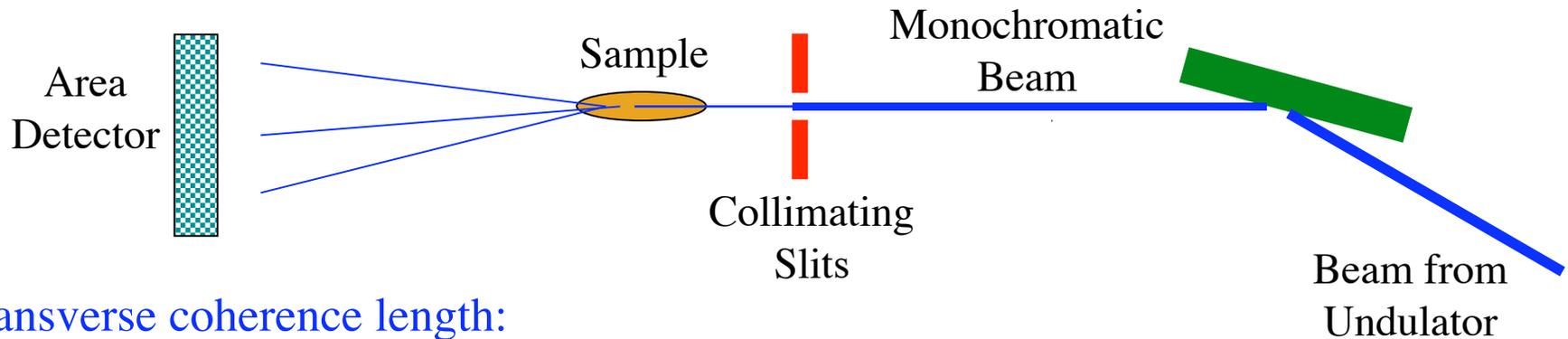
- Fluctuations of Smectic Membranes
- Capillary Waves on Polymer Films
- Diffusion in Magnetorheological Elastomers
- Concentration Fluctuations in Binary Fluids
- Unmixing in Metal Alloys

### Wide Angle

- Charge Density Wave Motion in  $\text{NbSe}_3$
- Domain Motion in  $\text{Co}_{0.6}\text{Ga}_{0.4}$



## Generating the coherent beam:



### Transverse coherence length:

$$\xi = \sqrt{R/2\lambda} \sim 10 \text{ } \mu\text{m}$$

- Slit Aperture  $\lesssim \xi$

source to sample distance:  $R \sim 50 \text{ m}$

x-ray wavelength:  $\lambda \sim 1 \text{ } \text{\AA}$

source size:  $\sim 100 \text{ mm}$

### Longitudinal coherence length:

$$\xi = \lambda^2 / \Delta E$$

- Path Length Variation  $\lesssim \xi$

spectral width:  $(\Delta E/E) \sim 10^{-4}$

## Key Ingredients:

- Source:
- Highly Brilliant
  - Highly Stable

- Beamline Optics:
- Brilliance Preserving
  - Stable
  - Clean

# Multispeckle XPCS

$$\text{Average over Pixels} = \text{Ensemble Average}$$

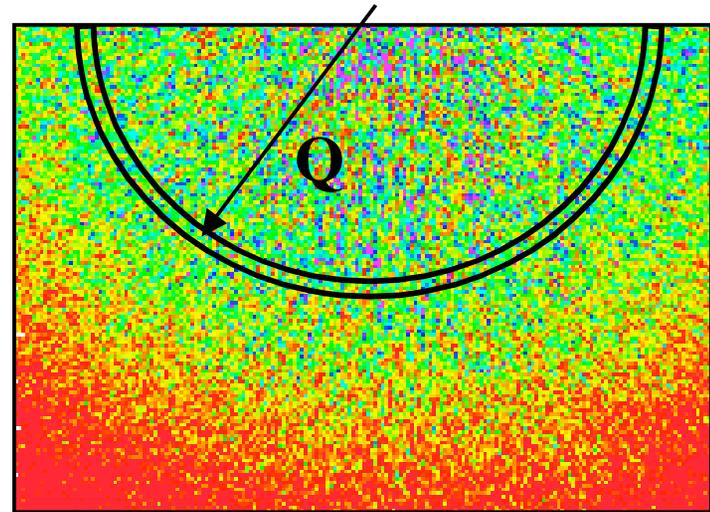
Demanding Tolerances for Area Detector

- Throughput (Time Resolution)
- Spatial Resolution
- Quantum Efficiency

Key for Low Count Rates

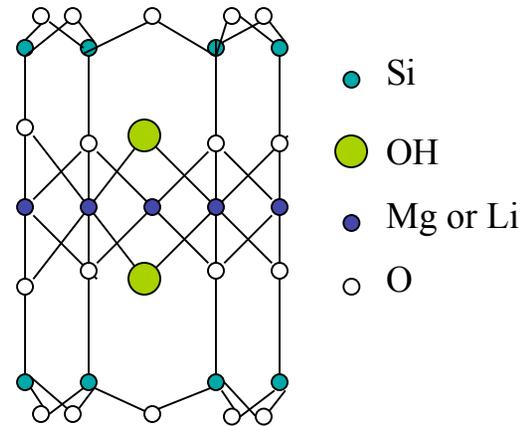
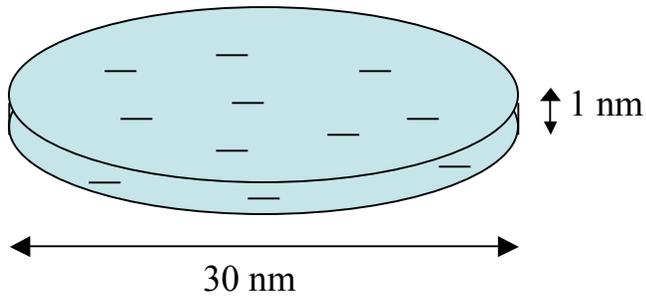
Crucial for Non-Ergodic Systems

e.g., Glasses, Clay Gels

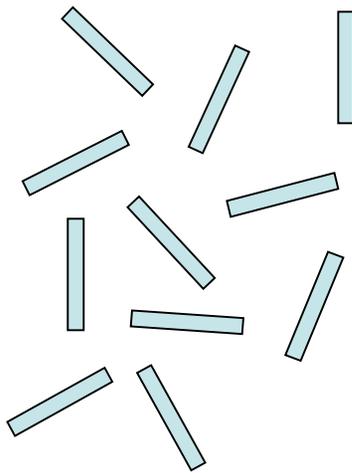


# Laponite: A Synthetic Clay.

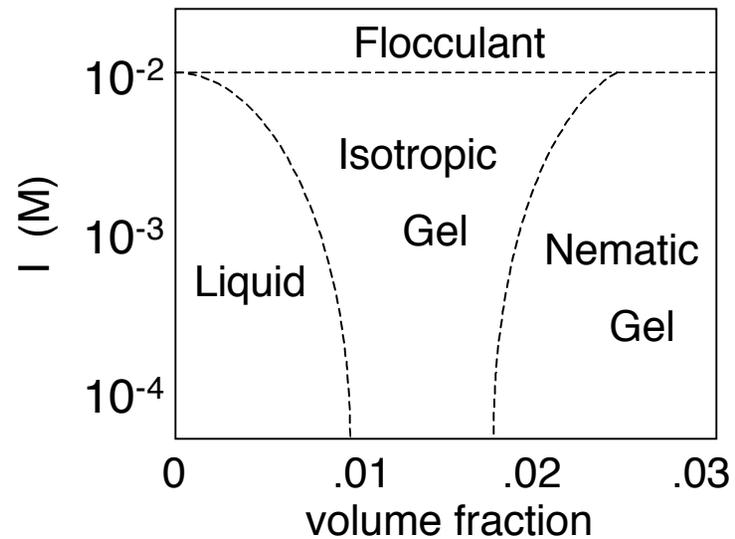
Charged Disks...



...in Aqueous Solution...

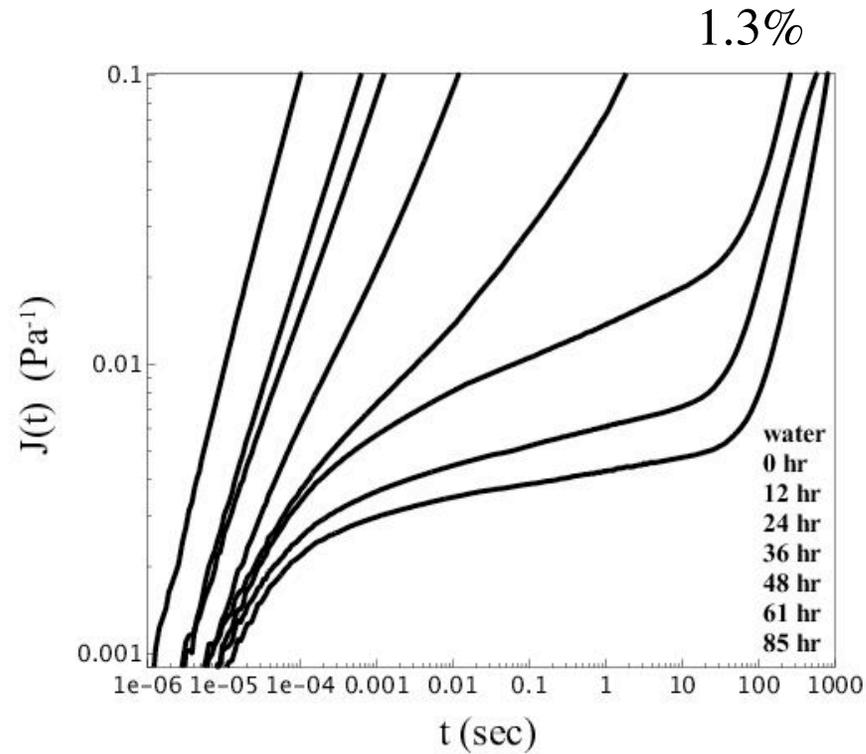


...Form Soft Solids.



# Evolution of Viscoelastic Behavior.

Creep Compliance:



- Slow Transformation from Liquid to Solid.
- Rate Strongly Density Dependent.

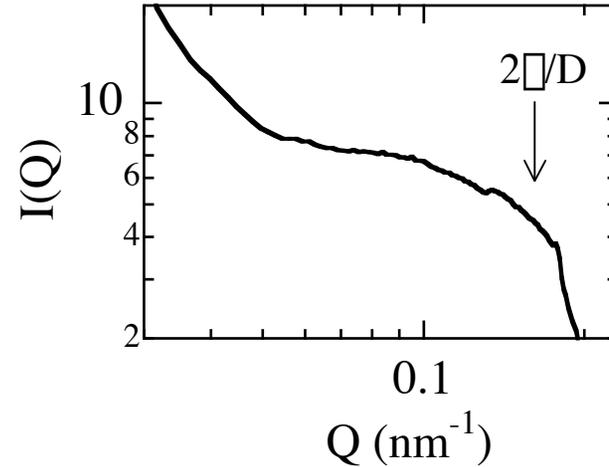
# XPCS: Probe of the Local Dynamics.

Over Wave Vector Range:

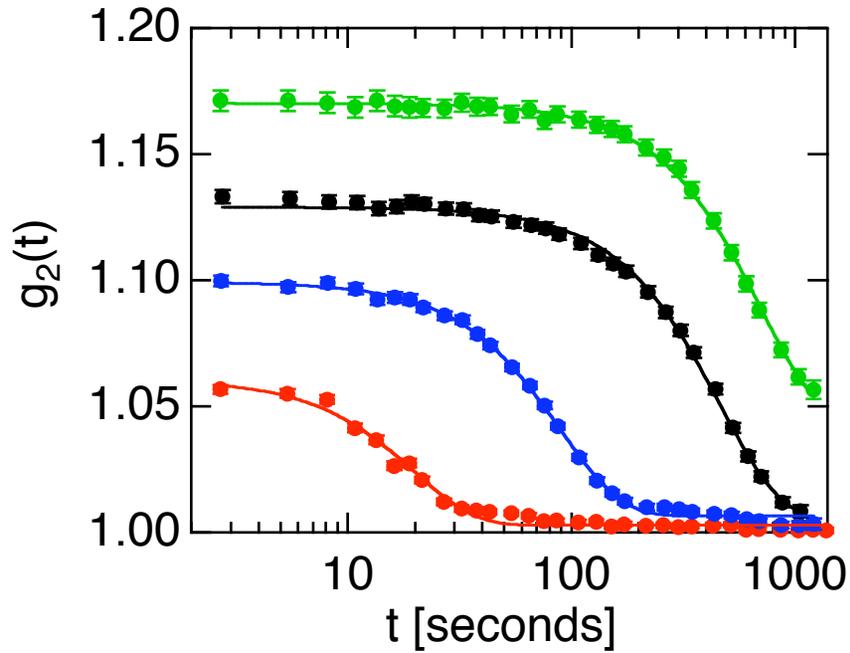
$$0.03 \text{ nm}^{-1} < Q < 0.3 \text{ nm}^{-1}$$

Motion Progressively Slows

Static Structure:



$Q = 0.14 \text{ nm}^{-1}$



age (s)

13000

30000

90000

200000

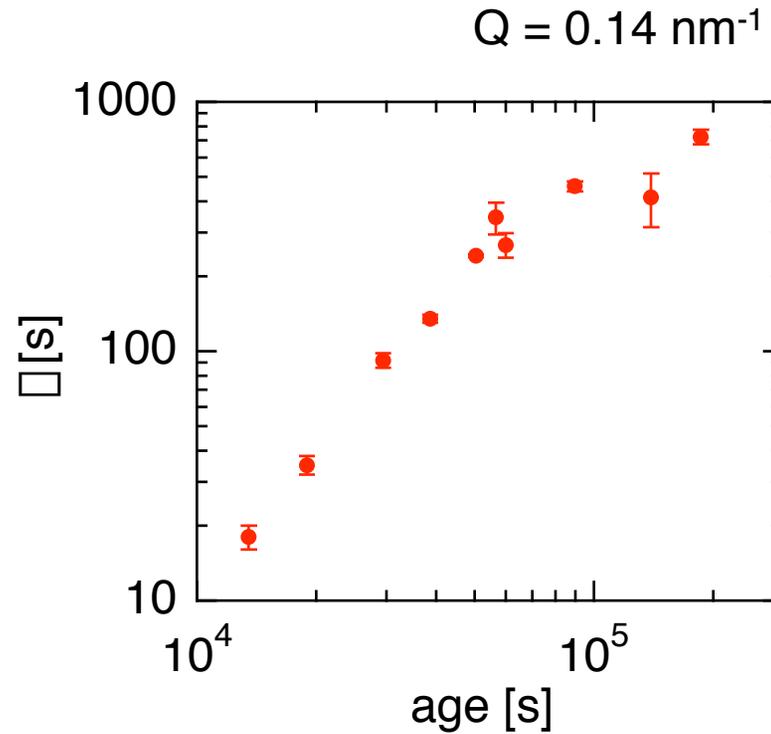
Correlations Fit to:

$$g_2(t) = A \exp\left(-\left(\frac{t}{\tau}\right)^{\alpha} + 1\right)$$

## Growth of Correlation Times.

- Varies with Density.
- Follows Scaling:

$$\tau \sim t_a^\alpha, \quad \alpha \approx 1$$

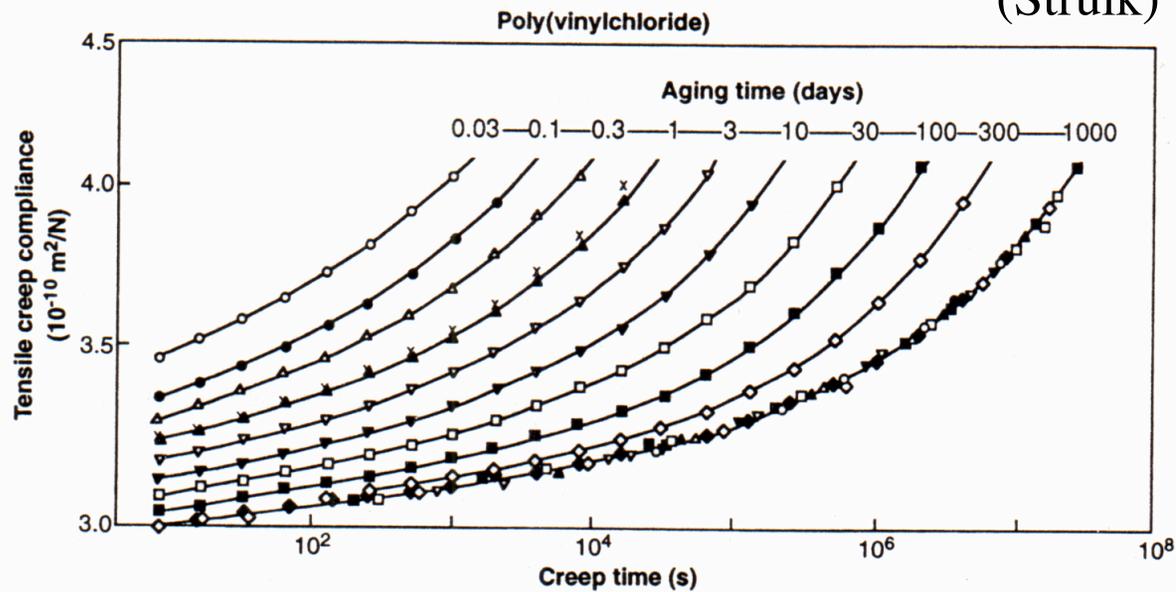


- Such Scaling Ubiquitous in Aging Systems.  
e.g., Polymer Glasses, Spin Glasses.
- Relevance?

## “Classic” Aging Behavior:

Eg., Creep compliance of polymer melts below  $T_g$ .

(Struik)



$$\square = C t_a$$

However, for Particle-Scale Dynamics:

Glasses

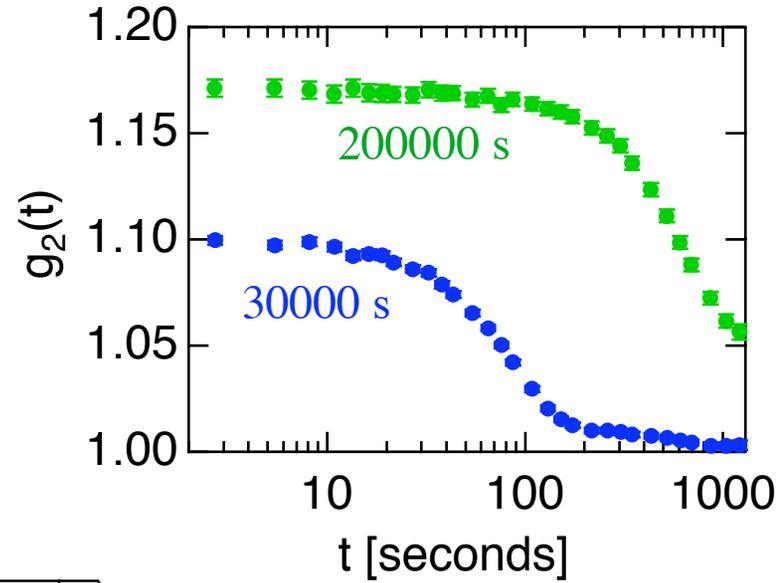
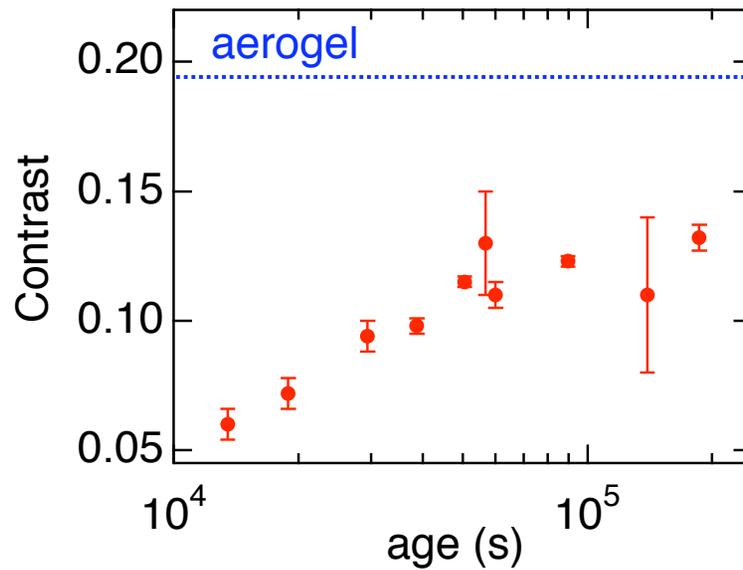
$$C > 10^3$$

Clay Gel:

$$C < 10^{-2}$$

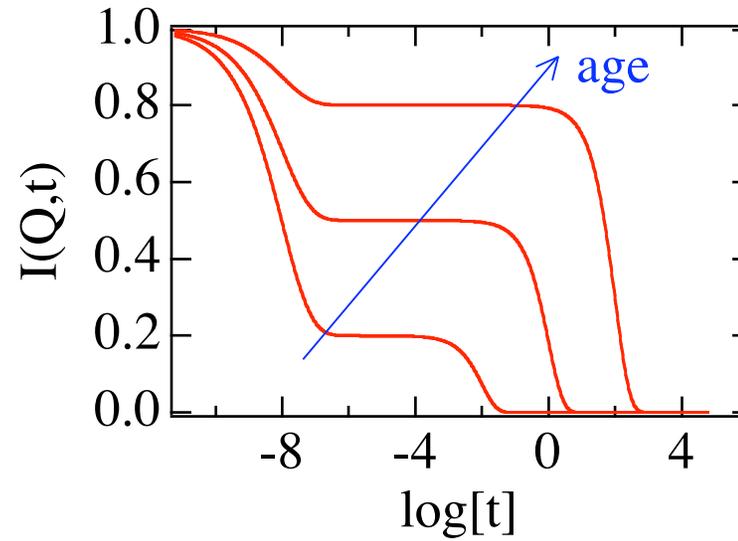
## Apparent Contrast:

Increases Quasi-Logarithmically:

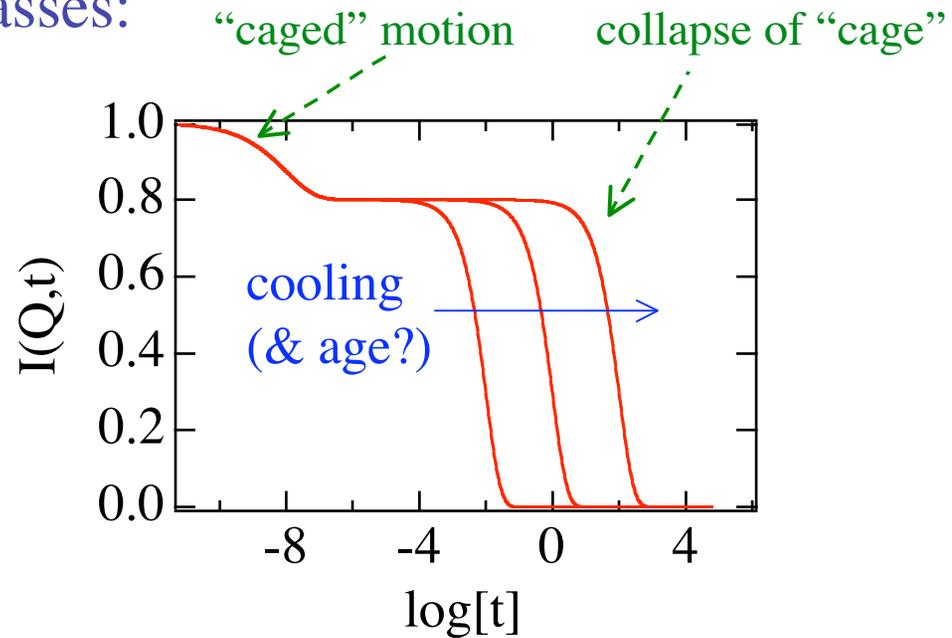


Implications?

## Two Step Relaxation in Laponite:



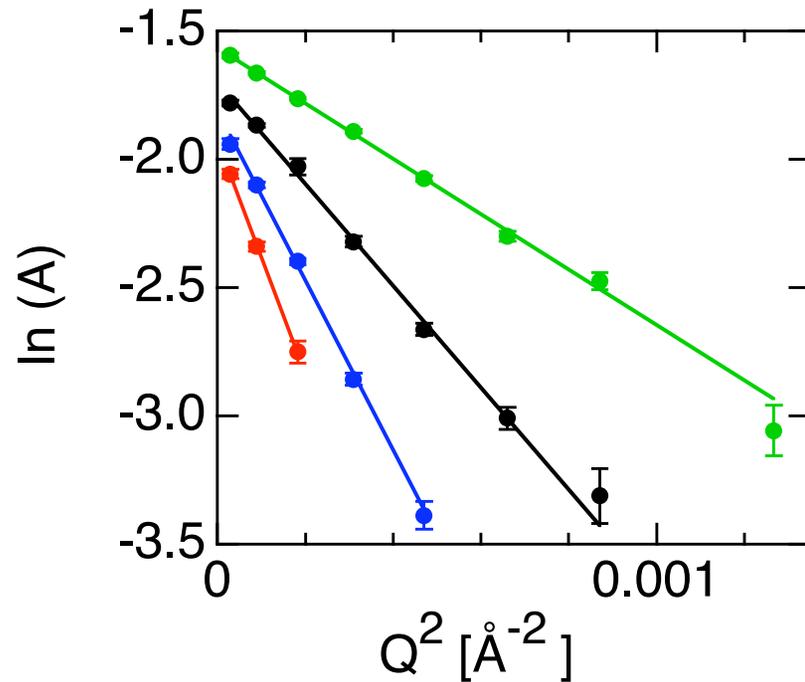
## Typical Behavior for Glasses:



## Q dependence of Step Amplitude

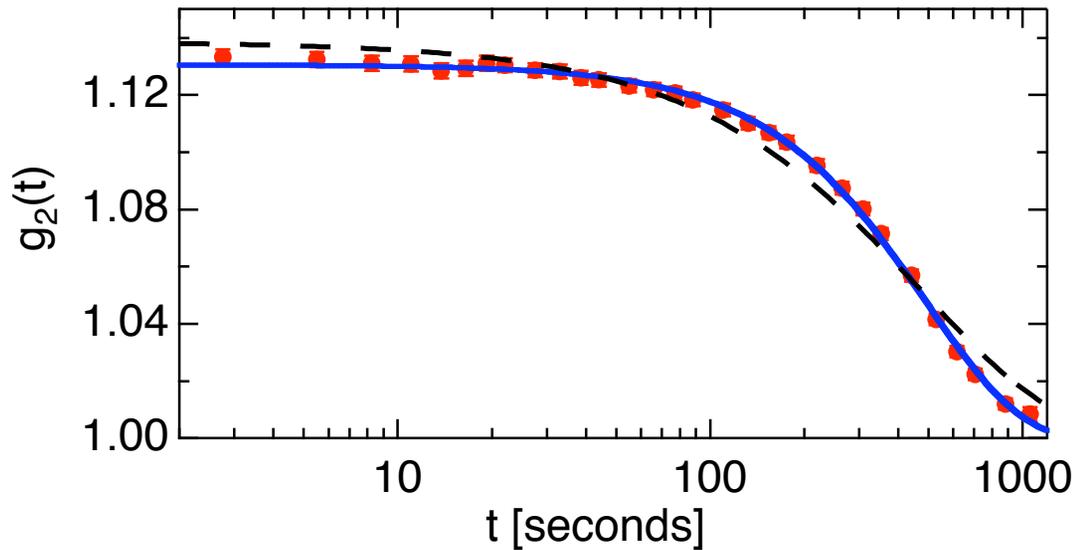
A Measure of Cage Size.

Within Cage Picture One Can Argue:  $A \sim \exp(-\langle r^2 \rangle Q^2/3)$



age [s]	$\langle r^2 \rangle^{1/2}$ [nm]
13000	12
30000	10
90000	7.8
200000	5.7

## Evolution of Correlation Function:



$$g_2(t) = A \exp\left[-\left(\frac{t}{\tau}\right)^{\beta} + 1\right]$$

At Small Age,  $\beta \approx 1$

At Large Age,  $\beta \rightarrow 1.5 - 1.7$

Precedence in an Aggregating Colloidal System (Cipelletti et al.).

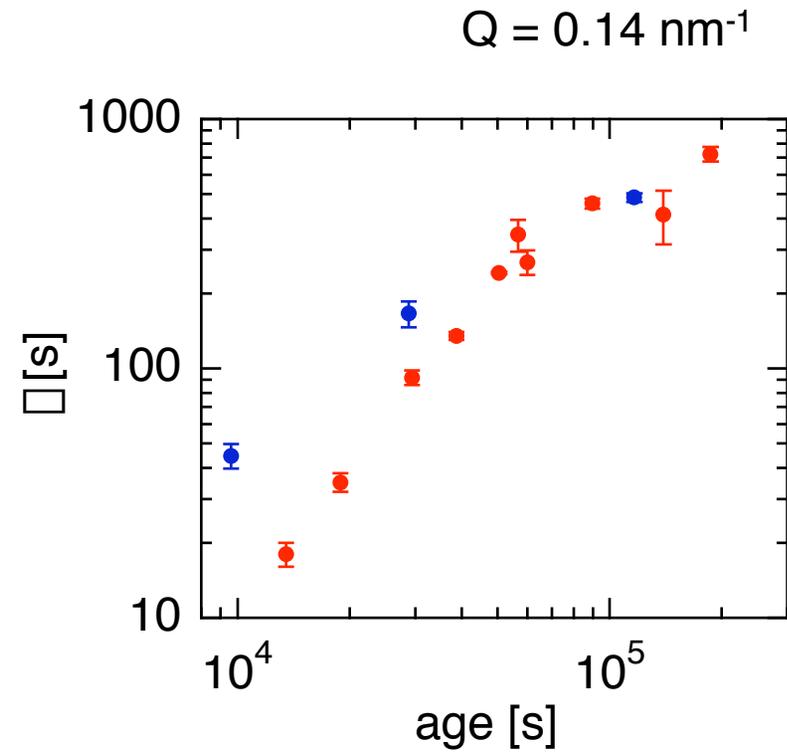
- Small Angle DLS ( $10^{-5} < Q < 10^{-3} \text{ nm}^{-1}$ ).
- Modeled in terms of strain fields from “micro-collapses”.  
(Bouchaud and Pitard)

# Rejuvenation

Reinitialize Aging.

Glasses: Temperature Cycle

Laponite: Shear



## Future Directions of Our Research:

XPCS as Probe of “Soft Glassy Materials”.

eg., Nanocomposites: Clay + polymers, Liquid Crystals + Colloids.

Objectives:

Connection between Glassy Rheology and Particle-Scale Dynamics.

Microscopic Perspective on Aging.